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Combination effect of organically modified montmorillonite and layered nickel hydroxide on the fire retardancy of poly(lactic acid)

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Abstract

The combination effect of organically modified montmorillonite (OMT) and layered nickel hydroxide ($Ni(OH)_2$) on the fire retardancy of poly(lactic acid) (PLA) was reported. Thermogravimetric analysis and microscale combustion calorimeter were used to evaluate the thermal stability and fire retardancy of the PLA nanocomposites. Direct pyrolysis/mass was employed to investigate the thermal degradation behaviors of the PLA nanocomposites. The char residues of the PLA nanocomposites were characterized by X-ray diffraction and Raman spectroscopy. After the incorporation of OMT and $Ni(OH)_2$ into PLA, the decomposition temperature occurred earlier but improved char residue was obtained. The combination of OMT and $Ni(OH)_2$ led to a significant reduction in the heat release rate and total heat release of PLA as compared to the individual component. The presence of OMT was beneficial for the formation of gas and liquid species from PLA with lower molecular weight. As for the char residues of the PLA nanocomposites, the combination of OMT and $Ni(OH)_2$ contributed to the highest graphitization degree. It was metallic Ni *in situ* reduced from $Ni(OH)_2$ that acted as the catalytic role of graphitization.

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Keywords: Poly(lactic acid); Fire retardancy; Thermal degradation; Catalytic carbonization

1. Introduction

Poly(lactic acid) (PLA) as a group of biodegradable polymers has received much attention for its wide application in pharmaceutical [1], and as a packing materials [2]. PLA is regarded as a promising alternative to conventional plastics because it is facilely available from renewable sources such as starch, potato, and other agricultural products [3], has low toxicity and has high mechanical performance. However, just like other plastics, the high flammable property of PLA severely restrains its certain application. Much attention has been paid to the field of biodegradbility, but only little work has been done about the flame retardancy of PLA up to now.

Traditional halogen-containing compounds used as flame retardants are more and more unpopular because plenty of smoke and toxic gases are produced during combustion, which are very harmful to human health and the environment. Therefore, some efficient halogen-free flame retardant systems for PLA are investigated. Intumescent flame retardants are considered as promising additives to reduce the flammability of PLA due to their many advantages including high efficiency, low smoke, and low toxicity [4]. PLA nanocomposites, especially PLA/layered silicate nanocomposites, have attracted great interest because they exhibit good flame retardancy at a low loading and low cost, and are environmentally friendly [5]. The synergistic effect between organoclay (OMT) and other flame retardants on the flammability of polymers is on the focus in recent years because of the high flame retardant efficiency. A previous study by Tang et al reported that

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the fire retardancy of polymers could be greatly improved through strengthening char forming by use of the nickel oxides in combination with OMT [6]. Clay-based polymer nanocomposites with Lewis acid-type transition metal chlorides showed synergistic flame retardant effects because a surface-protective layer having a clay network structure was formed and enhanced char formation was obtained using the catalyst [7].

In this article, PLA nanocomposites with OMT and/or $Ni(OH)_2$ were prepared via direct melt compounding. The thermal stability and fire retardancy of the PLA nanocomposites were evaluated by thermogravimetric analysis (TGA) and microscale combustion calorimeter (MCC). The thermal degradation behaviors of PLA nanocomposites were investigated by Direct pyrolysis/mass (DP-MS). The resultant char residues of the PLA nanocomposites were characterized by X-ray diffraction (XRD) and Raman spectroscopy. A possible synergistic mechanism of OMT and $Ni(OH)_2$ on the flame retardancy of PLA was proposed based on these observations.

2. Experimental section

2.1. Materials and preparation method

PLA was supplied by Cargill Dow. OMT was prepared from montmorillonite (MMT, a kind of layered silicates owning to the family of 2:1 phyllosilicates) by ion exchange reaction using hexadecyl trimethyl ammonium bromide in water. Layered nickel hydroxide ($Ni(OH)_2$) was prepared through a co-precipitation method according to the published literature [8]. PLA, OMT and $Ni(OH)_2$ were dried in vacuum at 80 °C overnight before use. PLA was firstly melt-mixed with 8wt% OMT in a twin-roller mill (KX-160, Jiangsu, China) at a temperature of 170 °C for 8 min, then a proportional $Ni(OH)_2$ (4wt%) was added into the above system until a good dispersion was achieved.

2.2. Characterization

TGA experiments were performed using a Q5000 IR thermoanalyzer instrument, in which the specimens (about 10 mg) were heated to 700 °C at a heating rate 20 °C/min. A Govmark MCC-2 microscale combustion calorimetry (MCC) was used to determine the flammability characteristics of PLA composites according to ASTM D 7309-07. DP-MS analysis was carried out with a Micromass GCT-MS spectrometer using the standard direct insertion probe for solid polymer materials at a heating rate of 15 °C/min. Raman spectroscopy measurements were carried out at room temperature with a SPEX-1403 laser Raman spectrometer (SPEX Co, USA).

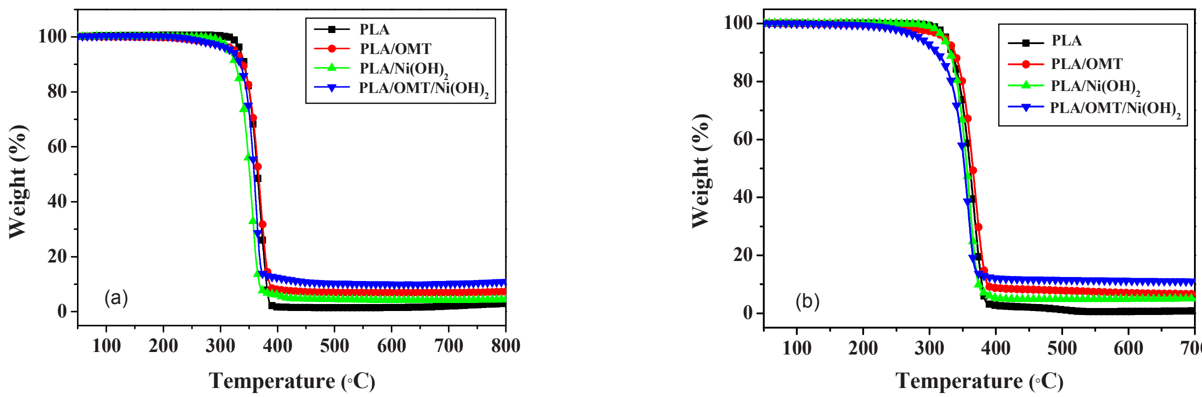

Fig. 1. TGA curves of the PLA nanocomposites in N_2 (a) and air (b).

3. Results and discussion

3.1. Thermal stability of the PLA nanocomposites

The thermal degradation behaviors of the PLA nanocomposites are examined by TGA as shown in Fig. 1. The thermal degradation of all PLA samples appears to occur in one step in the temperature range between 300 and 400 °C. In all cases both the initial decomposition temperature ($T_{-5\%}$) and the maximum decomposition temperature (T_{max}) for PLA containing OMT and/or $Ni(OH)_2$ occur at a slightly lower temperature than those of pure PLA. It is worth to mention that

PLA/OMT/$Ni(OH)_2$ has the highest char residue of 10.2 wt% at 700 °C, which indicates that the combination of OMT and $Ni(OH)_2$ benefits the char formation during combustion. Similar TGA results for the PLA nanocomposites are observed in an air atmosphere. There is few char residue left for pure PLA in air, but the addition of OMT and $Ni(OH)_2$ into PLA gives rise to a high amount of char residue of about 11.0 wt%.

3.2. Fire retardancy of the PLA nanocomposites

The fire retardancy of the PLA nanocomposites is measured by MCC, which has become one of most efficient method for investigating the combustion property of polymers. Only one peak heat release rate (pHRR) is observed for all the samples in Fig. 2. The incorporation of OMT or $Ni(OH)_2$ lonely has a slight effect on reducing the pHRR of PLA, from 459.2 J/g.K of pure PLA to 339.6 J/g.K of PLA/OMT or to 404 J/g.K of PLA/$Ni(OH)_2$. A synergistic effect of OMT and $Ni(OH)_2$ on reducing the flammability of PLA is observed with the lowest pHRR of 260 J/g.k.

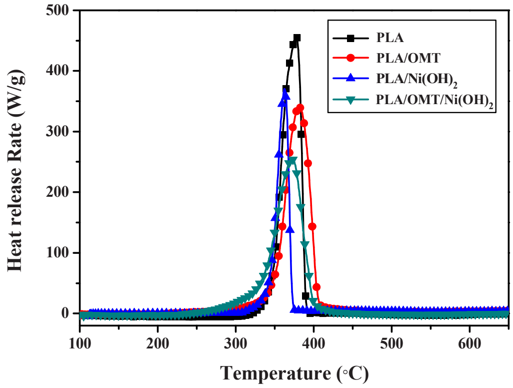

Fig. 2. The curve of heat release rate versus temperature for the PLA nanocomposites.

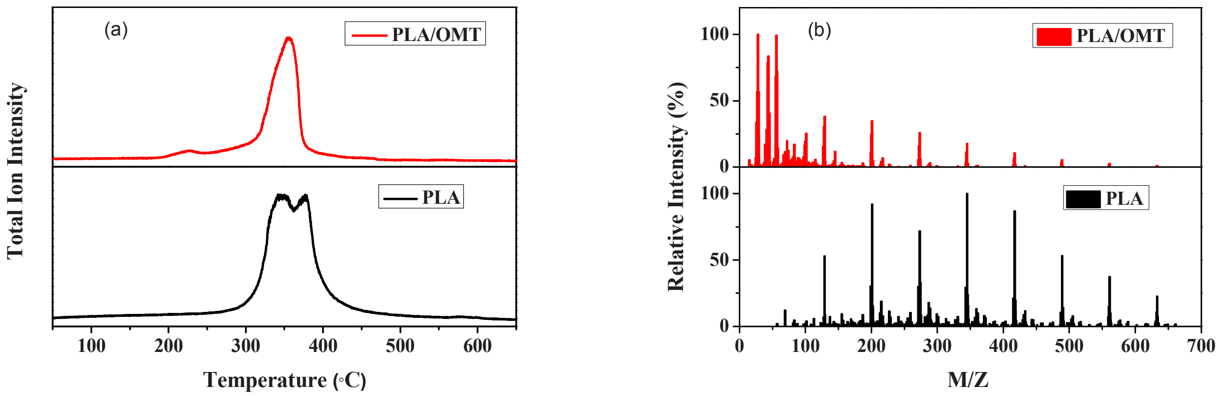

Fig. 3. (a) TIC curves of the decomposition process of PLA and PLA/OMT; (b) MS spectra of compounds evolved from PLA and PLA/OMT at the same temperature.

3.3. Thermal decomposition mechanism of the PLA nanocomposites

DP-MS is used to confirm the role of OMT on the thermal degradation of PLA. Fig. 3a shows the total ion current (TIC) chromatograms of PLA and PLA/OMT, and the mass spectra (MS) corresponding to the TIC peaks are presented in Fig. 3b. The main pyrolytic products consist of acetaldehyde, acrylic acid, lactoyl acrylic acid, lactide isomers, and cyclic oligomers [9, 10]. There is a wide molecular weight distribution of pyrolytic products of PLA in the range of 15-778. By comparison, the components with lower molecular weight are found in the mixture of pyrolytic components of PLA/OMT. In this sense, the presence of OMT promotes the formation of pyrolytic components of PLA with lower molecular weight.

Raman spectroscopy is used to characterize the graphitization degree of char residues of the PLA nanocomposites (Fig. 4). The peak at about 1595 cm^{-1} called G band is a characteristic of sp^2-bonded crystalline carbon, while the D band centered at around 1355 cm^{-1} is assigned to amorphous carbon and lattice defects. The intensity ratio of G and D band (I_G/I_D) is measured to estimate the degree of graphitization and an increasing I_G/I_D value corresponds to a relatively perfect crystallinity [11]. Seen from Fig. 4, the I_G/I_D ratio follows the sequence of PLA/$Ni(OH)_2$ (0.506) < PLA/OMT (0.514) < PLA/OMT/$Ni(OH)_2$ (0.734). The thermal stability of PLA is improved by combination of OMT and $Ni(OH)_2$ through enhancing graphitization degree of the char.

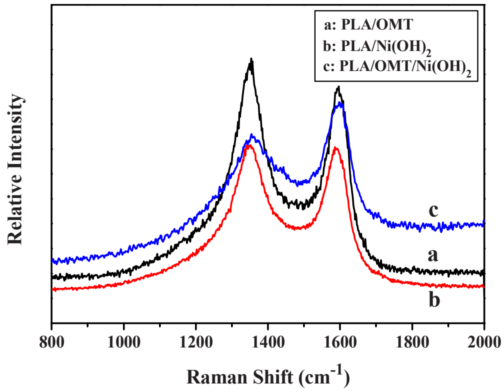

Fig. 4. (a) Raman spectra of the char residues of the PLA nanocomposites.

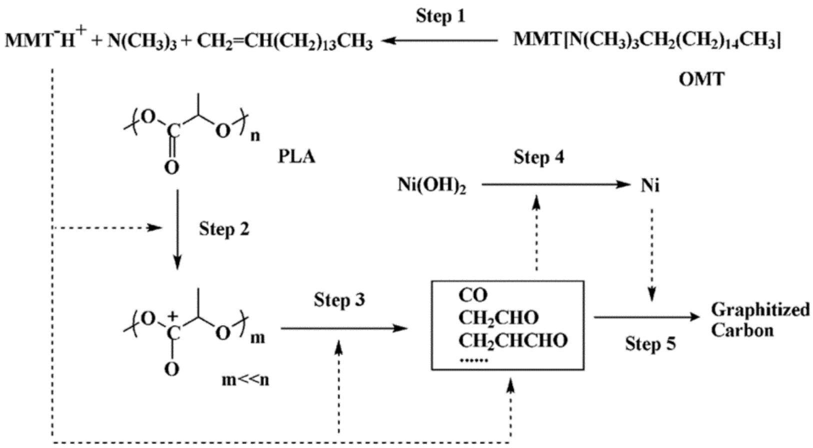

Fig. 5. Scheme for illustrating the combination effect of OMT and $Ni(OH)_2$ on reducing the flammability of PLA.

3.4. Scheme for the combination effect of OMT and $Ni(OH)_2$ on flame retardant PLA

Based on the above analysis and related reports, the combination effect of OMT and $Ni(OH)_2$ on reducing the flammability of PLA is depicted in Fig. 5. When heated at high temperature, the proton acidic sites are generated from the decomposition of modifier on the degraded OMT layers [12]. Once produced, the proton acidic sites are beneficial for producing cationic active sites, which will accelerate the degradation of PLA [9]. The catalytic degradation of PLA by OMT could promote the formation of gas and liquid species with lower molecular weight. Thanks to the barrier property of clays, the pyrolytic products are constrained in the system with lower volatilization [13]. Nickel nanoparticles are *in situ* formed through the reduction of $Ni(OH)_2$ by the small species (XRD data not shown), which will act the catalytic sites for converting the small species into graphited char. Thus, the combination of OMT and $Ni(OH)_2$ accompanies with improved yield and graphitization degree of char residue.

4. Conclusions

The combination of $Ni(OH)_2$ with OMT could significantly reduce the heat release rate and total heat release of PLA. The incorporation of OMT benefits the formation of pyrolytic species from PLA with lower molecular weight, which would be further graphitized under the influence of $Ni(OH)_2$. The combination of OMT and $Ni(OH)_2$ accompanies with improved charred residue yield and graphitization, which is responsible for the improved fire retardancy of PLA.

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